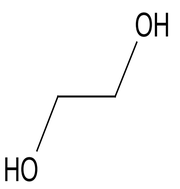
**Nagaphani Kumar Batchu, Koen Binnemans**

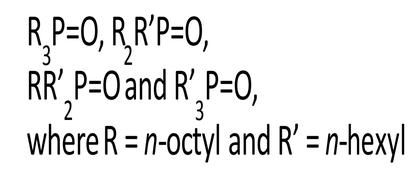
Laboratory of Inorganic Chemistry, KU Leuven-University of Leuven
Celestijnenlaan 200F, P.O.box 2404, 3001 Heverlee, Belgium
nagaphanikumar.batchu@chem.kuleuven.be

# Non-aqueous solvent extraction of rare-earths ions

Solvent extraction is defined as the preferential distribution of a solute between two immiscible liquid phases.[1] Traditionally, water or aqueous solutions are being one of these two liquid phases. But it is always not necessary. The requisite condition is that the two liquid phases must be immiscible with each other. It is possible to prepare two immiscible liquid phases without aqueous solutions for solvent extraction of metals. [2,3] The replacement of aqueous phase by organic solvents leads to new branch of extractive metallurgy called solvometallurgy. For instance, solvent extraction of cobalt and nickel has been studied using two mutually immiscible ionic liquid phases, 1-ethyl-3-methylimidazolium chloride, and trihexyl(tetradecyl) phosphonium bis(2,4,4-trimethylpentyl)phosphinate.




Ethylene glycol



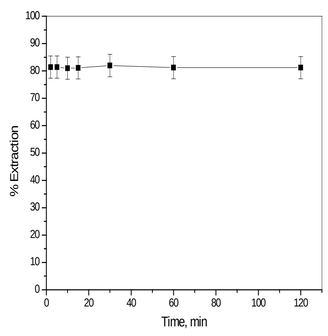

Cyanex 923

## Aim

To study the solvent extraction of Nd(III) from two immiscible organic solvents phase system namely ethylene glycol(+$LiNO_3$) as more polar organic phase and trialkylphosphine oxide (Cyanex 923) diluted in dodecane as less polar organic phase

## Extraction Kinetics

The major objective of non-aqueous solvent extraction is to exploit the difference in solvation of metal ions in non-aqueous solvents in order to achieve high extraction efficiency and separation factors. The physical parameters of the solvents such as viscosity, and density plays important role in extraction kinetics. It was found that equilibrium was very fast and achieved in 2 minutes.




◀ Effect of equilibration time on the extraction of Nd(III) from ethylene glycol medium. Experimental Conditions: [Nd(III)] = 6.07 × $10^{-3}$ M, EG, [$LiNO_3$] = 1 M, [Cyanex 923] = 0.05 M, RT, Stirring speed = 1200 rpm, Time = 2-120 min.

## Extraction mechanism

- Ethylene glycol was co-extracted at higher concentrations of Cyanex 923
- No phase volume changes after the extraction.
- The slope of plot of log D verses log[Cyanex 923] indicates three moles of Cyanex 923 involving the extraction reaction.
- The distribution ratio of Nd increases with increase in the nitrate ion concentration suggesting the participation of nitrate ion in the extracted complex.

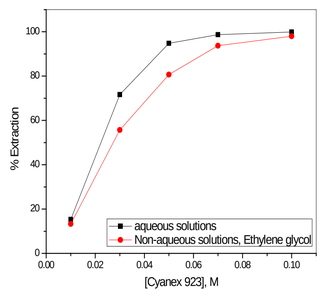
The solvent extraction reaction can be represented as

$R + EG \rightarrow R{\cdot}EG$ (1)

$Nd^{3+} + 3\ NO_3^- + 3\ R{\cdot}EG \rightarrow Nd(NO_3)_3.3R{\cdot}EG$ (2)

where EG represents ethylene glycol and R represents Cyanex 923.

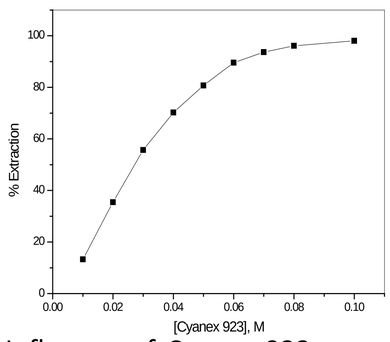
## Comparison of extraction from aqueous solutions



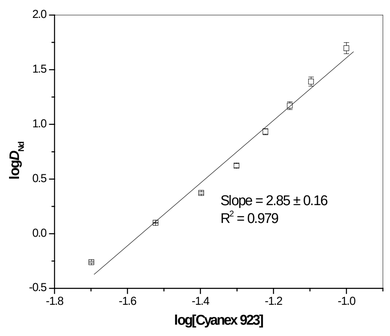

➢ The activity of cation is suppressed in the non-aqueous solvent environment leads to low extraction of the metal to less polar organic phase

▲ Comparision of extraction of Nd(III) from aqueous and ethylene glycol solutions using Cyanex 923. Experimental Conditions: [Nd(III)] = 6.28 × $10^{-3}$ M, [$LiNO_3$] = 1 M, [Cyanex 923] = 0.05 M.

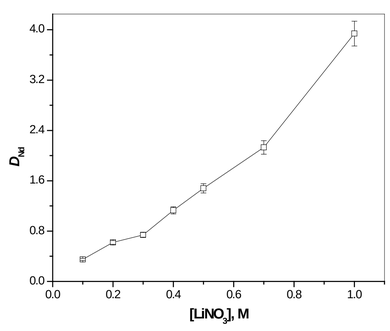
## Extraction parameters




▲ Influence of Cyanex 923 concentration on the distribution ratio of Nd(III). [Nd(III)] = 7.53 × $10^{-3}$ M in ethylene glycol (EG), [LiNO3] = 1 M, [Cyanex 923] = 0.01-0.1 M.



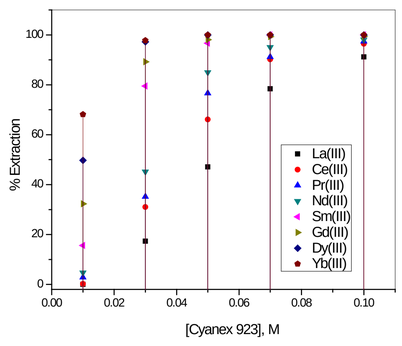

▲ Variation of distribution ratio of Nd(III) as a function of Cyanex 923 concentration. Experimental Conditions: [Nd(III)] = 7.53 × $10^{-3}$ M in EG, [$LiNO_3$] = 1 M, [Cyanex 923] = 0.01-0.1 M.




◀ Variation of distribution ratio of Nd(III) as a function of nitrate ion concentration. [Nd(III)] = 7.01 × $10^{-3}$ M in EG, [$LiNO_3$] = 0.1-1 M, [Cyanex 923] = 0.05 M

## Extraction of other rare earths

- The extractabilities of heavy rare-earths are high compared to light rare-earths.
- This phenomenon was similar to the behavior of rare earths in aqueous solutions.
- There is a possibility of group separation of heavy rare-earths from light rare-earths at 0.03 M Cyanex 923 indicated by a separation factor of 79.6 for (Yb+Dy) over (La+Ce+Pr+Nd).




▲ Effect of Cyanex 923 on the extraction of rare earths. [RE(III)] = 6.07 × $10^{-4}$ M in EG(each), [$LiNO_3$] = 1 M, [Cyanex 923] = 0.01- 0.1 M

## Conclusion

A new solvent extraction system that is free of aqueous solutions comprising ethylene glycol and dodecane was developed. The systematic solvent extraction study of Nd(III) from ethylene glycol medium using Cyanex 923 diluted in dodecane was reported. The extraction efficiency of Nd(III) increased with increase in Cyanex 923 concentration and nitrate ion concentration. The solvent extraction reaction was proposed on the basis of slope analysis.

[1] J. Rydberg, M. Cox, C. Musikas and G. R. Choppin, Solvent Extraction: Principles and Practice, Marcel Dekker, Inc., New York, 2nd edn, 2004.
[2] A. Rout, S. Wellens, K. Binnemans, *RSC Advances* **4**, 5753–5758 (2014).
[3] A. Rout and K. Binnemans, *Dalton Transactions* **43**, 3186–3195 (2014).